ADSORPTION AND DIFFUSION OF ALCOHOL VAPORS FOR ARGONNE PREMIUM COALS

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INTRODUCTION

Green and Selby reported [1] that pyridine sorption isotherms can be explained by a dual-mode sorption model that has been widely applied to the sorption of glassy polymers. This model is represented by two phenomena, adsorption on the surface described by a Langmuir isotherm, predominant at the initial portion of the plot of sorption isotherm, and diffusion (absorption) into the bulk structure described by Henry's law, the linear portion with relative pressures. Shimizu et al. [2] carried out research on organic vapor sorption using various ranks of coals and found that sorption data for Illinois No. 6 coal could be treated by the Langmuir–Henry equation regardless of a kind of the organic vapors (methanol, benzene, pyridine, and cyclohexane) used. Takanohashi et al. [3] reported that methanol sorption in the residues from coals with the high extraction yields greatly increased compared to the corresponding raw coals, suggesting that more microporosity has been developed by the extraction. In contrast, for coals with low extraction yields, sorption behavior of residues was similar to that of the raw coals, regardless of coal rank.

The steric effects on the kinetics of solvent swelling of coals have been reported.[4,5] Solvent swelling of coal involves diffusion of solvent molecules into the macromolecular structure of coals. Larsen et al. [4] reported the steric effects of various alkyl-substituted pyridines and anilines on equilibrium swelling ratio of coals. Aida et al. [5] determined the initial swelling rates in addition to the equilibrium swelling values of Illinois No.6 coal in various solvents, and showed that the rate retardation of diffusion of alkyl-substituted amines can be increased by almost a thousandfold by changing from n-butylamine to $tert$-butylamine. However, the swelling of coal in liquid phase also causes other structural changes such as extraction and relaxation of macromolecular structure, which can influence the swelling behavior.

To investigate the steric effect on alcohol vapor sorption for coals, the sorption isotherms of alcohols with different size of alkyl groups were measured for four Argonne premium coal samples. Data were analyzed using the Langmuir–Henry dual-mode sorption equation. Based on the adsorption and diffusion parameters from the model equation, micropore and cross-linking structures of the coals are discussed.

EXPERIMENTAL

Sample Preparation
Four Argonne premium coal samples (Pocahontas No.3, Upper Freeport, Illinois No.6, and Beulah-Zap coals) were obtained in ampoules (5 g of -150 μm). Because water and gases adsorbed on the coals prevent the measurement of sorption, samples were dried at 80 °C for 12 h in $vacuo$, just before the sorption measurements. Various alkyl-substituted alcohols were used without further purification as the sorbate.

Upper Freeport coal was extracted exhaustively with a carbon disulfide / N-methyl-2-pyrrolidinone (CS_2 / NMP) mixed solvent at room temperature.[6] The residue was washed with acetone and dried in a vacuum oven at 80 °C for 12 hr. The extraction yield was 60 wt% on the dry-ash free basis. The extraction residue was also used as the sorbent.

Sorption Experiments
Sorption isotherms were measured with an automatic vapor adsorption apparatus (BELSORP18, BEL JAPAN, INC) at 30 °C. Approximately 200 mg of sample was placed in the sample tube and weighed. The deaeration treatment of methanol in the solvent tank was carried out with liquid

nitrogen three times through freeze-thaw cycles. Samples were pretreated under vacuum ($< 10^{-4}$ Torr) at 80 °C for 12 h: The sorption isotherm was measured at the relative vapor pressures of 0.01 $< p < 1$ at 30 °C by using the constant-volume gas adsorption method. Each sorption was measured when the change in the amount of sorption remained constant within 5% for 10 min.

RESULTS AND DISCUSSION

Sorption Behavior.
Sorption isotherms of methanol, ethanol, n-propanol and n-butanol (only for Upper Freeport coal) are shown in Figures 1. The amount of sorption is represented on the basis of each sample (g). Generally, the sorption increased exponentially at low vapor pressures and then increased linearly with pressure in the intermediate pressure range, although the total sorption was different among the coals used. The sorption by Upper Freeport raw coal was the smallest for all alcohols used. As the size of alkyl group increased, the total sorption became smaller for all coals, showing that alkyl groups prevent the alcohols from being sorbed by the coals. For lower rank coals, Beulah-Zap and Illinois No.6 coals, the sorption behaviors of methanol and ethanol were similar at vapor pressures more than 0.2, i.e., the slope of isotherm was almost the same. While, for high rank coals, Upper Freeport and Pocahontas No.3 coals, the slope of isotherms in the cases of n-propanol and n-butanol was relatively small, indicating that they would hardly be sorbed

Sorption Analysis Using the Dual-Mode Sorption Model
The results of curve fitting from the Langmuir – Henry dual mode equation (1) are also shown in Figure 1.
$$C = C_H + C_D = C'_H b p / (1 + b p) + k_D p \qquad (1)$$
where C is the total sorption (mmol/g-sample), C_H is adsorption on the surface, C_D is the amount of diffusion (absorption) into the bulk, C'_H is the pore saturation constant, b is the pore affinity constant, p is the relative vapor pressure (P/P_0), and k_D is the Henry's dissolution constant.

For all the cases except for Beulah-Zap – ethanol and n-propanol systems, data were fit by the Langmuir–Henry equation, suggesting that alcohol sorption can be explained by adsorption on the surface that occurred at low relative pressures and diffusion into the bulk that increased linearly with pressure. Since coals have many interacting sites such as functional groups on their surface, adsorption preferentially occurs at low vapor pressure. A steep increase of sorption observed for all coals at low vapor pressures, especially for low rank coals, can be due to the adsorption on oxygen functional groups of the surface, although in the case of n-propanol the rate of the sorption increase at low vapor pressures was small.

Constants of the Langmuir–Henry equation obtained by the fitting are listed in Table 1. The values for Beulah-Zap – ethanol and n-propanol systems were obtained by a different fitting method, i.e., the adsorption parameter was obtained by fitting in the low vapor pressure range less than 0.2 and the diffusion parameter by fitting in the intermediate pressure range more than 0.4, because a discontinuity point exists at around vapor pressure of 0.2. The C'_H (mmol/g-sample) for Upper Freeport coal was the smallest for all alcohols, showing that Upper Freeport coal has fewer pores on the surface than other coals. As the size of alkyl group increased, i.e., methyl, ethyl and propyl, the C'_H decreased, especially for high rank coals the rate of decrease was large. The result suggests that high rank coals have smaller micropore sizes. The b which is related to the ratio of the adsorption rate to the desorption rate, showed a tendency to decrease in the cases of n-propanol and n-butanol. The steric effect of alkyl group of alcohols may accelerate their desorption.

The Henry's dissolution constant k_D (mmol/g-sample), which represents the degree of diffusion into the bulk, was also the smallest for Upper Freeport coal in all cases. For low rank coals, the k_D values of methanol and ethanol were similar, while the value of n-propanol was small. In contrast, for high rank coals k_D greatly decreased in the order of methanol, ethanol and propanol, suggesting that the difference in the size of alkyl group on alcohols might greatly influence their diffusion into the bulk.

Effect of Extraction
Figure 2 shows the isotherms for Upper Freeport residue, with the Langmuir–Henry fitting curves. Constants of the Langmuir–Henry equation obtained by the fitting are also listed in Table 1. The C'_H of each alcohol for the raw coal and its extraction residue was almost similar in magnitude, although the value of methanol for the residue was smaller than that for the raw coal. The values of b increased by the extraction for all alcohols. In contrast, the k_D for the residue was quite larger than that for the raw coal in all cases. Even for bulky alkyl-substituted alcohols such as n-propanol

and n-butanol, high the k_D values were obtained, 1.6 for both. These results suggest that the adsorption sites on the surface did not change so much by the extraction, while a considerable amount of large void was formed in the bulk. Since the oxygen content of the Upper Freeport residue, 6.3 wt%, is much lower than those for Illinois No.6 and Beulah-Zap raw coals, the increase in the k_D for the residue may be due to increased physical diffusion into the formed voids.

CONCLUSIONS

Almost all sorption isotherms of various alcohols could be explained by the Langmuir-Henry dual-mode sorption equation, and adsorption and diffusion parameters could be estimated. Both pore saturation and dissolution constants were the smallest for Upper Freeport coal of all coals used. As the size of alkyl group increased, their constants decreased for all coals. Especially for high rank coals, Pocahontas and Upper Freeport coals, the dissolution constant greatly dropped. In contrast, the dissolution constant for the extraction residue from Upper Freeport coal was quite large for all alcohols, compared to those of the raw coal, although the pore saturation constant did not change so much. A considerable amount of micropores with relatively large sizes formed by the extraction may be responsible for the increased diffusion.

ACKNOWLEDGMENT

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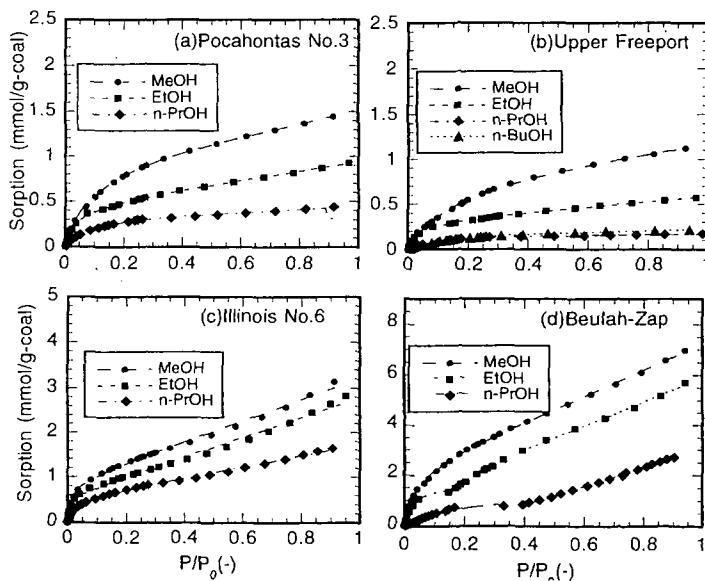6. Iino, M., Takanohashi, T., Ohsuga, H. and Toda, K., *Fuel*, **67**, 1639 (1988).

Figure 1 Sorption isotherms of various alcohols at 30 °C for Pocahontas No.3 (a), Upper Freeport (b), Illinois No.6 (c) and Beulah-Zap (d) coals, with the fitted lines with the Langmuir-Henry dual mode equation.

Table 1 The adsorption and diffusion parameters by Langmuir–Henry dual-mode sorption equation for the raw coal – alcohol systems and Upper Freeport extraction residue

coal	sorbate	$C'_H{}^a$ (mmol/g-coal)	b^b (-)	$k_D{}^c$ (mmol/g-coal)
Pocahontas No.3 raw	methanol	0.98	10	0.61
	ethanol	0.46	26	0.49
	n-propanol	0.35	12	0.12
Upper Freeport raw	methanol	0.81	35	0.79
	ethanol	0.30	30	0.29
	n-propanol	0.18	9	0.01
	n-butanol	0.20	7	0.05
Upper Freeport residue	methanol	0.58	55	3.1
	ethanol	0.33	69	2.3
	n-propanol	0.35	35	1.6
	n-butanol	0.37	13	1.6
Illinois No.6 raw	methanol	0.97	58	2.9
	ethanol	0.66	108	1.9
	n-propanol	0.58	32	1.1
Beulah-Zap raw	methanol	2.3	29	5.0
	ethanol	1.7	39	4.8
	n-propanol	1.3	6	3.7

^{a} Pore saturation constant.　^{b} Pore affinity constant.　^{c} Dissolution constant.
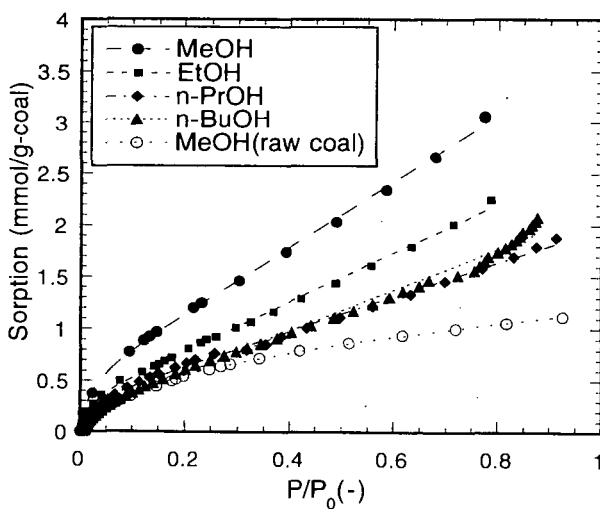
Figure 2 Sorption isotherms of various alcohols at 30 °C for Upper Freeport residue, with the fitted lines with the Langmuir-Henry dual-mode equation.